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Dielectric dispersion and relaxation mechanism of some polar molecules and their binary mixtures in benzene solutions at microwave frequencies

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Abstract . Dielectric Permittivity (ε') and dielectric loss (ε'') of pyridine, chlorobenzene, benzophenone, p-fluoroaniline and mixtures of pyridine + p-fluoroaniline, chlorobenzene + p-fluoroaniline and benzophenone + p-fluoroaniline have been measured at three different microwave frequencies 7.22, 9.1, 19.61 GHz at 30°C in benzene solution. The static permittivity at 455 KHz and refractive index were also measured. The most probable relaxation time (τ_0) and distribution parameter (α) have been determined from measured data using Cole-Cole method of analysis. The presence of intermolecular association through hydrogen bonding (N-H----N) was observed in the mixture of pyridine + p-fluoroaniline. The dielectric data for p-fluoroaniline and mixtures were analysed in terms of two relaxation times τ_1 and τ_2.

Keywords Dielectric relaxation, distribution parameter, hydrogen bonding

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1. Introduction

Relaxation parameters of polar liquid mixtures are affected by several factors *e.g.* the relaxation time of individual components, their dipole moments and interaction between them. Madan [1-5] studied some rigid polar molecules and their mixtures in dilute solutions and found that in mixture polarization order decays exponentially just as it does for single component system. Dielectric measurements carried out by Prakash and Rai [6] for mixtures of aniline + nitrobenzene at microwave frequencies suggested that the relaxation time of mixture is influenced by the presence of component which has larger value of relaxation time. Intermolecular association in polar liquid mixtures has been reported by several workers by relaxation as well as dipole moment studies [7-13]. We studied mixtures of o-chloroaniline with nitrobenzene and benzonitrile with aniline in benzene solution at different temperatures (at a single microwave frequency) and found that there is solute-solute/solvent type of interaction at low concentration of anilines [14,15]. With a view to gain more information in this area, we carried out dielectric measurements on pyridine, chlorobenzene, benzophenone, p-fluoroaniline and mixtures of pyridine + p-fluoroaniline, chlorobenzene + p-fluoroaniline and benzophenone + p-fluoroaniline at three different microwave frequencies in benzene solution at room temperature and the results are reported in this paper.

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2. Experimental details

Pyridine (AR grade) supplied by Sd Finechem Ltd. (India), chlorobenzene (AR grade) supplied by Sisco Research Lab (India), benzophenone (puriss for synthesis) supplied by Spectrochem Pvt. Ltd. (India) and p-fluoroaniline (for synthesis) supplied by Merck (Germany) were used without further purification. Benzene (AR grade) supplied by Qualigens (India) was used after fractional distillation. The mixtures of pyridine + p-fluoroaniline, chlorobenzene + p-fluoroaniline and benzophenone + p-fluoroaniline were prepared by taking polar components in equal mole. These mixtures were taken as solute and added to non-polar solvent. Five dilute solutions of pyridine, chlorobenzene, benzophenone, p-fluoroaniline and the mixtures were prepared by using benzene as non-polar solvent.

The dielectric permittivity (ε') and dielectric loss (ε'') at three different microwave frequencies 7.22, 9.1, 19.61 GHz were determined by the method suggested by Heston *et al* [16],

adopted for short circuited termination. The static permittivity ε_0 at frequency 455 KHz was determined by resonance method, which uses a tuned oscillator circuit and standard variable capacitor. ε_∞ was taken as a square of refractive index which was measured by Abbe's refractometer. All the measurements were carried out at 30°C and the temperature was controlled thermostatically to within ± 0.5°C.

3. Results and discussion

The slopes a_0, a', a'', a_∞ determined by plotting the measured values of ε_0, ε', ε'' and ε_∞ against weight fraction of solute in solution for single component and their binary mixtures at different frequencies are listed in Table 1. a'' has been plotted against a' on complex plane to evaluate the most probable relaxation times (τ_0). Fairly smooth curves could be drawn passing through the experimental points. For pyridine, chlorobenzene and benzophenone a Debye type plot with center on the x-axis is observed (Figure 1), whereas for p-fluoroaniline and for mixtures a Cole-Cole type of plot with center below x-axis is observed (Figure 2). The most probable relaxation time (τ_0) and distribution parameter (α) for pyridine, chlorobenzene and benzophenone are presented in Table 2. The values of relaxation time increase with the size of molecule and are in close agreement with literature values. The zero values of distribution parameter (α) for these molecules suggest a simple Debye type relaxation mechanism for these systems, which is usual behavior of rigid polar molecules. In comparison to pyridine, chlorobenzene and benzophenone, less data is available in literature on dielectric measurement of p-fluoroaniline. Dhar *et al* [22] studied p-fluoroaniline at different temperatures and 3 cm wavelength in benzene solution, the value of relaxation time for this compound reported by them is 5.1 ps at 30°C. The values of relaxation time 5.3 ps (Table 2) for p-fluoroaniline in the same solvent and at the same temperature in the present work is in close agreement with their value of relaxation time. The value of distribution parameter (α) for p-fluoroaniline (Table 2) is finite (0.20). Srivastava and Vij [23] studied o-chloro, m-chloro, and p-chloroanilines in benzene solution, they found finite distribution parameter for these molecules and further, the distribution parameter shown an increasing trend from o- to m- to p- isomers. The value of distribution parameter for p- chloroaniline determined by them at 30°C was 0.25, thus the value of distribution parameter (α)

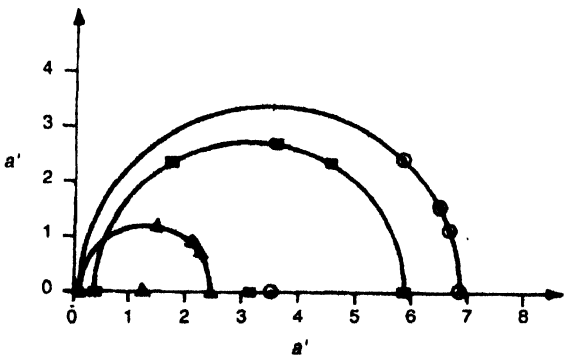

Figure 1. Plots of a'' *versus* a' for pyridine (O), chlorobenzene (Δ) and benzophenone (□) in benzene solution.

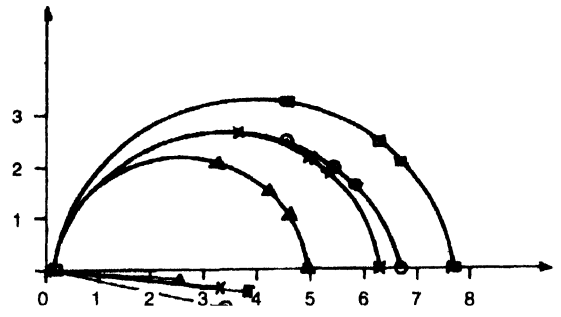

Figure 2. Plots of a'' *versus* a' for p-fluoroaniline (O), mixtures of pyridine + p-fluoroaniline (□), chlorobenzene + p-fluoroaniline (Δ) and benzophenone + p-fluoroaniline (×) in benzene solution

Table 1. Values of slopes a_0, a', a'' and a_∞ of single component as well as their binary mixtures in benzene solution at different frequencies at 30°C

	Frequency							
	455 KHz	7.22 GHz		9.1 GHz		19.61 GHz		Optical
Substance	a_0	a'	a''	a'	a''	a'	a''	a_∞
Pyridine	6.87	6.67	1 10	6.50	1 50	5 85	2 40	0 07
Chlorobenzene	2 43	2.23	0.63	2 10	0 74	1 50	1.10	0.15
Benzophenone	5 87	4 50	2.36	3.58	2.70	1.70	2 37	0.35
p-Fluoroaniline	6.59	5 83	1 68	5.50	2.05	4 54	2 48	0 15
Pyridine + p-Fluoroaniline	7.55	6.75	2.09	6 25	2.38	4 50	3 08	0 19
Chlorobenzene + p-Fluoroaniline	4 92	4.58	1.14	4.25	1 50	3.28	2 10	0.19
Benzophenone + p-Fluoroaniline	6.25	5.40	2.00	5 10	2.30	3 63	2 70	0 29

for p-fluoroaniline (0.20) in present work appears reasonable. This finite value of distribution parameter (α) for p-fluoroaniline suggest that there is more than one relaxation processes in this system. As suggested by several workers, for aniline and these parameters are given in Table 3. The value of relaxation time (τ_2) is 2.5 ps for p-fluoroaniline which may be attributed to rotation of – NH_2 group and is fairly in agreement with the literature values [27, 28].

Table 2. Values of distribution parameter (α), relaxation time (τ_0) and free energy of activation (ΔF_r) of the single component as well as their binary mixtures in benzene solution at 30°C

Substance	Distribution parameter (α)	Relaxation time (τ_0) in ps	Free energy of activation (ΔF_r) kCal/Mol	Relaxation time in ps (Lit values)
Pyridine	0.00	3 7	1 90	3.8 (ref 17) 3 56 (ref 18) 3 1 (ref 5) 3 2 (ref 20)
Chlorobenzene	0 00	7 5	2 32	7 8 (ref 19) 7 7 (ref 20) 8 3 (ref 21)
Benzophenone	0 00	14 1	2 70	16 0 (ref 3) 17 4 at 20°C (ref 21)
p-Fluoroaniline	0 20	5 3	2 11	5 1 (ref 22)
Pyridine + p-Fluoroaniline	0 07	6 6	2 25	
Chlorobenzene + p-Fluoroaniline	0 03	6 0	2 19	
Benzophenone + p-Fluoroaniline	0 10	7 8	2 34	

substituted anilines this may be due to rotation of $-NH_2$ group around its bond with the benzene ring. This has also been reflected in the value of relaxation time of p-fluoroaniline. The relaxation time of fluorobenzene found by us in our previous studies in benzene solution at 30°C is 5.7 ps [24], whereas that of p-fluoroaniline in the same solvent and at the same temperature is 5.3 ps. Although the molecular size of p-fluoroaniline is greater than that of fluorobenzene still its relaxation time is less which also suggest that there is an intramolecular rotation in p-fluoroaniline. Therefore, the dielectric data was analysed in terms of two relaxation times τ_1 and τ_2 where τ_1 and τ_2 are relaxation times corresponding to overall and group rotations respectively. In terms of a_0, a', a'' and a_∞ the Budo's [25] equation can be written for two relaxation processes as

$$\frac{a'-a_\infty}{a_0-a_\infty} = \frac{c_1}{1+\omega^2\tau_1^2} + \frac{c_2}{1+\omega^2\tau_2^2} \quad (1)$$

$$\frac{a''}{a_0-a_\infty} = \frac{c_1\omega\tau_1}{1+\omega^2\tau_1^2} + \frac{c_2\omega\tau_2}{1+\omega^2\tau_2^2} \quad (2)$$

where $c_1 + c_2 = 1$, c_1 and c_2 are relative weights contributed by each processes to the dielectric absorption as a whole. τ_1, τ_2, c_1 and c_2 for p-fluoroaniline was determined using the method suggested by Bhattacharya *et al* [26]. The evaluated values of

Table 3. Values of resolved relaxation times and their relative weight factors for p-fluoroaniline and its mixtures with pyridine, chlorobenzene and benzophenone in benzene solution at 30°C

Substance	τ_1 in ps	τ_2 in ps	c_1	c_2
p-Fluoroaniline	20 2	2 5	0 32	0 68
Pyridine + p-Fluoroaniline	16 9	2 3	0 44	0 56
Chlorobenzene + p-Fluoroaniline	19 4	2 8	0 29	0 71
Benzophenone + p-Fluoroaniline	15 0	2 6	0 54	0 46

The values of relaxation times of the mixtures of p-fluoroaniline with pyridine, chlorobenzene and benzophenone are also presented in Table 2. It is evident from the Table 2 that for mixtures of p-fluoroaniline with chlorobenzene and benzophenone the relaxation time of mixtures are nearly average of the individual value of relaxation time of constituent molecules. This is manifestation of super imposed effect of the pair of two components, the wavelength of the maximum absorption of pairs lying near to each other, thus giving rise to a broader single relaxation peak, this is in agreement with our earlier studies for mixtures of rigid polar molecules [29].

In the case of mixtures of pyridine + p-fluoroaniline, the relaxation time of the mixture is 6.6 ps (Table 2) while that of its

components are 3.7 ps (pyridine) and 5.3 ps (p-fluoroaniline). Thus, the value of relaxation time of mixture is higher than that of its components. This indicates that interactive association is taking place between pyridine and p-fluoroaniline molecules through N-H---N type of hydrogen bond. Similar results were obtained for the mixture of pyridine + pyrole and pyridine + indole in dilute solutions by Tridula *et al* [17].

The value of distribution parameter (α) for all the three mixtures investigated is finite, but less than the distribution parameter of p-fluoroaniline ; this suggests that there is more than one relaxation processes in the mixture and further, p-fluoroaniline retains its identity in the mixture. It appears that the presence of rigid polar molecules in the mixture with p-fluoroaniline, produces internal field such that the motion of $-NH_2$ is slightly restricted. The dielectric data of these mixtures is also analyzed in terms of two relaxation processes. The relaxation times and their contribution were determined by the method described for p-fluoroaniline. The evaluated values of τ_1, τ_2, c_1 and c_2 for the mixtures are also presented in Table 3. It is evident from the Table 3 that the values of relaxation time for group rotation (τ_2) in all the mixtures is of the same order found for p-fluoroaniline, which suggest that the components in the mixtures retain their identity.

Free energy of activation ($\Delta F_\varepsilon^{\ddagger}$) evaluated using Eyring's equation [30] for single component as well as that for binary mixtures is listed in Table 2. It can be seen that in the mixtures of chlorobenzene + p-fluoroaniline and benzophenone +p-fluoroaniline, the free energy of activation lies between those of its components, whereas in the case of mixture of pyridine + p-fluoroaniline, the activation energy is higher than those for its components, this also suggests that there is a complex formation in this mixture.

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